

12

LEVEL

OFFICE OF NAVAL RESEARCH
Contract No. N00014-79-C-0700
Task No. NR 359-723

TECHNICAL REPORT NO. 3

AN IR SENSITIVE, REAL-TIME IMAGING TECHNIQUE
BASED ON A PHOTOELECTROCHEMICAL CELL

by

Ronald H. Micheels and R. David Rauh

Prepared for Publication
in
Applied Physics Letters

EIC Laboratories, Inc.
55 Chapel Street
Newton, Massachusetts 02158

December, 1981

DTIC
ELECTE
DEC 30 1981
S D D

Reproduction in whole or in part is permitted for
any purpose of the United States Government

Approved for Public Release; Distribution Unlimited

81 12 28 264

AD A108991

DTIC FILE COPY

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM	
1. REPORT NUMBER Technical Report No. 3	2. GOVT ACCESSION NO. AD-1100991	3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle) AN IR SENSITIVE, REAL-TIME IMAGING TECHNIQUE BASED ON A PHOTOELECTROCHEMICAL CELL		5. TYPE OF REPORT & PERIOD COVERED Technical Report	
		6. PERFORMING ORG. REPORT NUMBER	
7. AUTHOR(s) Ronald H. Micheels and R. David Rauh		8. CONTRACT OR GRANT NUMBER(s) N00014-79-C-0700	
9. PERFORMING ORGANIZATION NAME AND ADDRESS EIC Laboratories, Inc. 55 Chapel Street, Newton, MA 02158		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 359-723	
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research/Chemistry Program Arlington, VA 22217		12. REPORT DATE December, 1981	
		13. NUMBER OF PAGES 14	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED	
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report) Approved for Public Release: Distribution Unlimited		Accession For NTIS GRA&I <input checked="" type="checkbox"/> DTIC TAB <input type="checkbox"/> Unannounced <input type="checkbox"/> Justification	
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		By Distribution/ Availability Dist Special A	
18. SUPPLEMENTARY NOTES Submitted for Publication in Applied Physics Letters			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Photoelectrochemistry, Imaging, Gallium Arsenide, Silicon, Infrared microns			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A real-time imaging technique based on optical saturation phenomena in photoelectrochemical cells has been developed. The long wavelength spectral sensitivity of these devices extends to the bandgap energy of the semiconductor photoelectrode employed. An image resolution of 180μ and a response time of better than 100 msec has been obtained with an n-GaAs cell.			

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

415-2-2

There have been several recent reports of static imaging on semiconductor photoelectrodes by means of light-induced film formation¹⁻³ or etching⁴⁻⁶. We describe here a new real-time imaging technique based on optical saturation effects in a photoelectrochemical cell. The technique has been used to obtain real-time imaging on n-GaAs and n-Si photoelectrodes. Image rise and fall times on the order of 100 msec. have been observed, thereby permitting continuous imaging that is suitable for applications such as near infrared and visible laser beam location, alignment, and profile analysis.

The mechanism behind the photoelectrochemical imaging technique can be explained in terms of the properties of the liquid electrolyte-semiconductor junction. When a semiconductor electrode is immersed in a stabilizing redox-electrolyte, a rectifying junction is formed in the semiconductor and in the solution in the vicinity of the interface⁷. Photogenerated electron-hole pairs are separated by this junction which causes, respectively, either holes or electrons to be drawn to the surface of an n- or p-type semiconductor. These minority carriers, which are localized at illuminated areas of the semiconductor surface, can then react to oxidize or reduce the appropriate member of the redox couple in solution. The reverse reaction takes place at an inert counterelectrode which completes the regenerative photoelectrochemical cell.

A depletion of the reacting redox species at an illuminated semiconductor surface can result, if the light flux is sufficiently

high to exceed the diffusion rate of this species in the electrolyte. For example, an n-GaAs photoelectrode with an I_3^-/I^- redox couple at concentrations below 0.02M in propylene carbonate, will exhibit a leveling off of the photocurrent vs. light intensity curve, for intensities above 3mW/cm^2 , due to diffusion limitations⁸. When a light pattern is projected on a photoelectrode surface under such diffusion limited conditions, a concentration gradient image will be generated due to the localized depletion of the reacting redox species and an increase in the conjugate species. Such a concentration image can be visualized in two different ways. If the depleted member of the redox couple exhibits stronger absorption of visible light than the other species, then the image can be seen in the form of a color change. A second method of image visualization involves raster-scanning a focused HeNe laser beam over the semiconductor surface and observing localized decreases in photocurrent at areas illuminated by the projected image of interest. Such a laser scanned image can be viewed in the form of an x-y vs. intensity map on a CRT monitor. The localized decreases in photocurrent can be produced directly by the effects of the redox species depletion on the photoelectrode charge transfer process or by the indirect effect of attenuation of the probing HeNe beam. The latter process will dominate when a significant change in extinction coefficient occurs between the two members of the redox couple at the HeNe wavelength (632.8 nm). The spectral response ranges of such imaging systems will be very similar to those of solid state junction devices of the same materials. The

long wavelength response limit is determined by the bandgap energy, which extends into the near infrared for many semiconductors that have been employed in stabilized photoelectrochemical cells⁷.

The semiconductor materials used in this study were: n-GaAs, single crystal, Si-doped, (100) face, 0.0008-0.0007 Ω -cm; and n-Si, single crystal, P-doped, (111) face, 0.2-0.3 Ω -cm. The redox electrolytes used with n-GaAs and n-Si were respectively: 0.01M tetrabutylammonium iodide and 0.005M I_2 in acetonitrile (resulting in 0.005M I_3^- and I^-); and saturated ferrocene in propylene carbonate. Both of these solutions also contained 0.1M tetrabutylammonium tetrafluoroborate as an inert supporting electrolyte. The n-GaAs and n-Si wafers were held in a cylindrical teflon cell, in which a circular area 13mm in diameter was exposed to the electrolyte solution and to light through a quartz window. The thickness of the solution layer above the semiconductor surface was 4mm. A back pressure contact was made to the wafers with a layer of indium foil backed against a brass disk. A platinum wire counterelectrode was used. The semiconductors were etched just before use in the following solutions: n-GaAs - 1:1 H_2SO_4 /30% H_2O_2 and n-Si - concentrated HF.

The laser spot scanning system consisted of a 3mW HeNe laser, two General Scanning G100PD optical scanners, and a 50mm focal length plano-convex focusing lens. The $1/e^2$ diameter of the focused laser spot on the photoelectrode surface was 11 μ . White light images of an arrow target pattern were projected on the photoelectrode using a 100W tungsten halogen lamp as an illumination source and a Canon 55mm

focal length, fl.4 camera lens. Two-dimensional laser spot scanned images were viewed on an x-y mode storage oscilloscope, using the photocurrent signal from the cell to modulate the CRT beam intensity. Photocurrent was monitored through an Amel 551 potentiostat.

The visualization of a localized concentration gradient image by means of the color change between the two redox species was demonstrated with an n-Si based photoelectrochemical cell with a ferrocene/ferricenium redox couple. The redox electrolyte solution initially only contained ferrocene, which has a yellow color and on oxidation is converted to the ferricenium ion which has a dark blue color. A distinct blue image of the projected arrow target pattern was generated even in the absence of an electrical connection to the Si electrode. However, substantially higher imaging sensitivity was obtained when a positive bias voltage of about 1.5V was applied to the Si electrode with respect to the Pt counterelectrode. The observation of photoelectrochemical image formation in the absence of an external current path can be explained by the presence of localized surface eddy currents set up between adjacent illuminated and dark areas of the n-Si surface. This phenomenon has been previously observed in this laboratory during studies of photoelectrochemical metal film deposition on p-Si⁴. Direct photolysis of ferrocene was found to be insignificant from absorption measurements of the solution in a 2mm cuvette illuminated with the same arrow image. Imaging was also achieved with the laser spot scanning method, where the cell photocurrent is monitored as a function of the position of the focused laser spot. A resolution

of about 300 μ was obtained. Because of the large increase in extinction coefficient at 632.8 nm that occurs in the conversion of ferrocene to ferricenium, the primary mechanism for the photocurrent image formation is attenuation of the HeNe beam by localized high ferricenium concentrations. The image buildup time was less than 2 sec.; however, a period of about 1 minute was required for the image to disperse. The near infrared sensitivity of the n-Si system was demonstrated by detection of a circular spot of light from a light emitting diode (Xciton XC-88-PC) which emits about 0.5mW in the forward direction in a narrow band centered at 880 nm.

The most successful imaging system investigated, in terms of resolution and response time, was the n-GaAs photoelectrochemical cell with an I^-/I_3^- redox couple in acetonitrile. Figure 1 shows a laser scanned photocurrent image of a white light arrow pattern projected on the GaAs cell. Part of the circular cell aperture and the Pt counterelectrode can also be seen due to their masking of the beam. The resolution obtained is about 180 μ . A -0.16 V bias voltage was applied to the GaAs electrode with respect to the Pt counterelectrode, which maintained the average current during laser scanning at less than 1 μ A. As the scanned HeNe beam traverses the 4mm path through the electrolyte in the cell, only 7.5% is absorbed by the 0.005M I_3^-/I^- in solution. The amount of increased absorption due to the photoelectrochemical conversion of a small fraction of the I^- to I_3^- by the projected image should be negligible. It is therefore expected that the photocurrent image in Figure 1 is due to saturation of the charge transfer

process and is not a result of absorption of the HeNe beam by the photogenerated I_3^- .

The one-dimensional laser scan in Figure 2 shows that the decrease in photocurrent due to the projected image is about 31% by comparison with the decrease in current where the mask blocks the beam. This latter observation confirms that the image is not primarily due to optical absorption. Any photolysis of the I_3^- that might occur would lead to increased transmission of the HeNe beam, producing an increase in photocurrent. The width at half height of the image peak in the oscilloscope trace shown in Figure 2 corresponds to a distance of 240 μ , which implies a resolution of about 200 μ when the actual projected image width of 80 μ is deconvoluted. The resolution will be limited by diffusion processes in the solution and can probably be improved by varying the redox couple concentration, the solution viscosity, and the thickness of the solution layer over the semiconductor surface.

Figure 3 gives the photocurrent image response curve for the n-GaAs cell. The curve was constructed by measuring the image peak height from one-dimensional scan traces, such as shown in Figure 2, as a function of the projected image intensity. The response curve indicates a linear dynamic range of about 12:1. The lower intensity end of the curve is limited by irregularities in the n-GaAs crystal surface, primarily from the etching process, and by high frequency electronic noise. The response begins to saturate at the high intensity end of the curve. Better etching procedures and analog

noise filtering should significantly extend the lower detection limit of the curve and increase the useful dynamic range, provided the response remains linear.

The rise and fall times for photocurrent imaging on n-GaAs were determined by suddenly switching a stationary, focused HeNe laser spot in and out of line with a second HeNe spot scanned in one dimension. The stationary spot was only moved about 2mm away from the scanned line so as to maintain a constant level of total illumination on the crystal. Image rise and decay curves were produced with a boxcar integrator gated at the point in time where the fixed spot image occurs. These measurements were made at a scanning frequency of 20 Hz with a scan length of 5mm. The photocurrent image rise and fall curves were very similar, both exhibiting a fast initial decay/rise with an exponential time constant of approximately 75 msec and a slower component with a 3.2 sec time constant. The amplitudes of the fast and slow components were approximately equal for both the rise and fall curves.

The superior time response and resolution of the n-GaAs system may be explained by the shorter diffusion length in the n-GaAs and by the differences in the image formation mechanisms. In the n-Si system the photocurrent is sensitive to the absorption of the HeNe beam, by ferricenium, over its entire path through the electrolyte while for the GaAs system, the cell photocurrent only senses the depletion of I^- in a thin layer of solution in contact with the photoelectrode surface.

Devices employing the real-time photoelectrochemical imaging technique have potential applications in many areas where photodiode and pyroelectric array detectors are currently employed. These new photoelectrochemical devices have a significant advantage in their simplicity and ease of fabrication. Studies employing the real-time imaging technique described here should also be able to provide new insights into the dynamics and transport phenomena occurring in photoelectrochemical cells.

This work was supported by the Office of Naval Research.

REFERENCES

- ¹T. Inoue, A. Fujishima and K. Honda, Chem. Lett. (Chem. Soc. Japan), 1197 (1978); J. Electrochem. Soc., 127, 1582 (1980).
- ²R. H. Micheels, A. D. Darrow II and R. D. Rauh, Appl. Phys. Lett. 39, 418 (1981).
- ³B. Reichman, F. R. F. Fan and A. J. Bard, J. Electrochem. Soc., 127, 333 (1980).
- ⁴L. V. Belyakov, D. N. Goryachev and M. N. Mizerov and E. L. Portnoi, Sov. Phys. Tech. Phys., 19, 837 (1974).
- ⁵R. W. Haynes, G. M. Metzger, V. G. Kreismanis and L. F. Eastman, Appl. Phys. Lett., 37, 344 (1980).
- ⁶F. W. Ostermayer, Jr. and P. A. Kohl, Appl. Phys. Lett., 39, 76 (1981).
- ⁷see for example: A. Heller, Acc. Chem. Res., 14, 154 (1981).
- ⁸R. D. Rauh, M. E. Langmuir, J. McHardy, R. H. Micheels, P. A. Hoenig, M. A. Parker and D. R. Pratt, Quarterly Tech. Prog. Report No. 3, SERI Subcontract XP-9-8002-7, May, 1980.

FIGURE CAPTIONS

- Fig. 1 Oscilloscope trace displaying a laser raster-scanned photocurrent image of an arrow pattern projected on an n-GaAs photoelectrode. The vertical scan rate is 5 Hz.
- Fig. 2. Oscilloscope trace of photocurrent vs. laser spot position for a one-dimensional scan across tail of arrow pattern (negative peak in center) and a tape mask on the cell window (broad negative peak on right). Horizontal scale is 0.8 mm/div. and vertical scale is 1.5 μ A/div. Scan rate is 5 Hz.
- Fig. 3. Photocurrent image response curve for n-GaAs cell.



2 mm

Figure 1



Figure 2

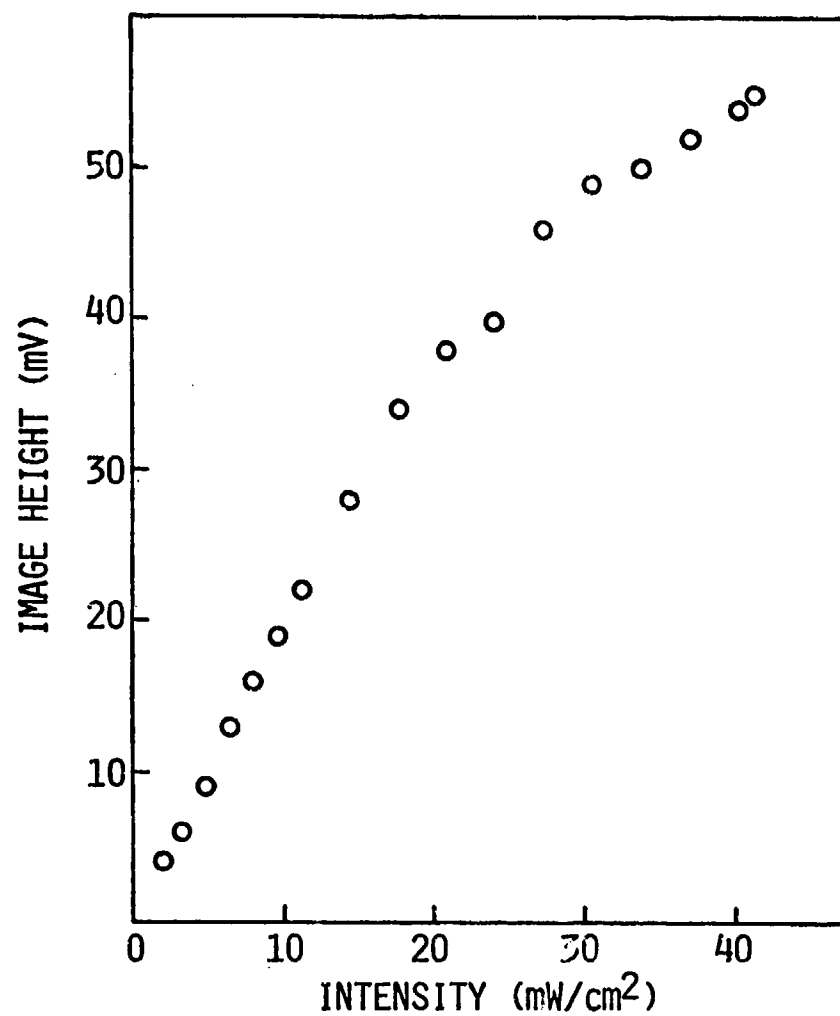


Figure 3

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Office of Naval Research Attn: Code 472 800 North Quincy Street Arlington, Virginia 22217	2	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 1211 Research Triangle Park, N.C. 27709	1
ONR Branch Office Attn: Dr. George Sandoz 536 S. Clark Street Chicago, Illinois 60605	1	Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
ONR Area Office Attn: Scientific Dept. 715 Broadway New York, New York 10003	1	Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	1
ONR Western Regional Office 1030 East Green Street Pasadena, California 91106	1	Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
ONR Eastern/Central Regional Office Attn: Dr. L. H. Peebles Building 114, Section D 666 Summer Street Boston, Massachusetts 02210	1	Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Director, Naval Research Laboratory Attn: Code 6100 Washington, D.C. 20390	1	Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
The Assistant Secretary of the Navy (RE&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1	Office of Naval Research Attn: Dr. Richard S. Miller 800 N. Quincy Street Arlington, Virginia 22217	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1	Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Naval Ocean Systems Center Attn: Dr. S. Yamamoto, Marine Sciences Division San Diego, California 91232	1
Dr. Fred Saalfeld Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1

TECHNICAL REPORT DISTRIBUTION LIST, GENNo.
Copies

Dr. Rudolph J. Marcus
Office of Naval Research
Scientific Liaison Group
American Embassy
APO San Francisco 96503

1

Mr. James Kelley
DTNSRDC Code 2803
Annapolis, Maryland 21402

1

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No. Copies</u>		<u>No. Copies</u>
Dr. Paul Delahay Department of Chemistry New York University New York, New York 10003	1	Dr. P. J. Hendra Department of Chemistry University of Southampton Southampton SO9 5NH United Kingdom	1
Dr. E. Yeager Department of Chemistry Case Western Reserve University Cleveland, Ohio 44106	1	Dr. Sam Perone Department of Chemistry Purdue University West Lafayette, Indiana 47907	1
Dr. D. N. Bennion Department of Chemical Engineering Brigham Young University Provo, Utah 84602	1	Dr. Royce W. Murray Department of Chemistry University of North Carolina Chapel Hill, North Carolina 27514	1
Dr. R. A. Marcus Department of Chemistry California Institute of Technology Pasadena, California 91125	1	Naval Ocean Systems Center Attn: Technical Library San Diego, California 92152	1
Dr. J. J. Auburn Bell Laboratories Murray Hill, New Jersey 07974	1	Dr. C. E. Mueller The Electrochemistry Branch Materials Division, Research & Technology Department Naval Surface Weapons Center White Oak Laboratory Silver Spring, Maryland 20910	1
Dr. Adam Heller Bell Laboratories Murray Hill, New Jersey 07974	1	Dr. G. Goodman Globe-Union Incorporated 5757 North Green Bay Avenue Milwaukee, Wisconsin 53201	1
Dr. T. Katan Lockheed Missiles & Space Co, Inc. P.O. Box 504 Sunnyvale, California 94088	1	Dr. J. Boechler Electrochimica Corporation Attention: Technical Library 2485 Charleston Road Mountain View, California 94040	1
Dr. Joseph Singer, Code 302-1 NASA-Lewis 21000 Brookpark Road Cleveland, Ohio 44135	1	Dr. P. P. Schmidt Department of Chemistry Oakland University Rochester, Michigan 48063	1
Dr. B. Brummer EIC Laboratories, Inc. 55 Chapel Street Newton, Massachusetts 02158	1	Dr. H. Richtol Chemistry Department Rensselaer Polytechnic Institute Troy, New York 12181	1
Library P. R. Mallory and Company, Inc. Northwest Industrial Park Burlington, Massachusetts 01803	1		

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Dr. A. B. Ellis Chemistry Department University of Wisconsin Madison, Wisconsin 53706	1	Dr. R. P. Van Duyne Department of Chemistry Northwestern University Evanston, Illinois 60201	1
Dr. M. Wrighton Chemistry Department Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1	Dr. B. Stanley Pons Department of Chemistry University of Alberta Edmonton, Alberta CANADA T6G 2G2	1
Larry E. Plew Naval Weapons Support Center Code 30736, Building 2906 Crane, Indiana 47522	1	Dr. Michael J. Weaver Department of Chemistry Michigan State University East Lansing, Michigan 48824	1
S. Ruby DOE (STOR) 600 E Street Washington, D.C. 20545	1	Dr. R. David Rauh EIC Laboratories, Inc. 55 Chapel Street Newton, Massachusetts 02158	1
Dr. Aaron Wold Brown University Department of Chemistry Providence, Rhode Island 02192	1	Dr. J. David Margerum Research Laboratories Division Hughes Aircraft Company 3011 Malibu Canyon Road Malibu, California 90265	1
Dr. R. C. Chudacek McGraw-Edison Company Edison Battery Division Post Office Box 28 Bloomfield, New Jersey 07003	1	Dr. Martin Fleischmann Department of Chemistry University of Southampton Southampton 509 5NH England	1
Dr. A. J. Bard University of Texas Department of Chemistry Austin, Texas 78712	1	Dr. Janet Osteryoung Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214	1
Dr. M. M. Nicholson Electronics Research Center Rockwell International 3370 Miraloma Avenue Anaheim, California 92800	1	Dr. R. A. Osteryoung Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214	1
Dr. Donald W. Ernst Naval Surface Weapons Center Code R-33 White Oak Laboratory Silver Spring, Maryland 20910	1	Mr. James R. Moden Naval Underwater Systems Center Code 3632 Newport, Rhode Island 02840	1

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No. Copies</u>		<u>No. Copies</u>
Dr. R. Nowak Naval Research Laboratory Code 6130 Washington, D.C. 20375	1	Dr. John Kincaid Department of the Navy Strategic Systems Project Office Room 901 Washington, DC 20376	1
Dr. John F. Houlihan Shenango Valley Campus Pennsylvania State University Sharon, Pennsylvania 16146	1	M. L. Robertson Manager, Electrochemical Power Sonics Division Naval Weapons Support Center Crane, Indiana 47522	1
Dr. M. G. Sceats Department of Chemistry University of Rochester Rochester, New York 14627	1	Dr. Elton Cairns Energy & Environment Division Lawrence Berkeley Laboratory University of California Berkeley, California 94720	1
Dr. D. F. Shriver Department of Chemistry Northwestern University Evanston, Illinois 60201	1	Dr. Bernard Spielvogel U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709	1
Dr. D. H. Whitmore Department of Materials Science Northwestern University Evanston, Illinois 60201	1	Dr. Denton Elliott Air Force Office of Scientific Research Bldg. 104 Bolling AFB Washington, DC 20332	1
Dr. Alan Berr Department of Chemistry The University Southampton, SO9 5NH England	1		
Dr. A. Himy NAVSEA-5433 NC #4 2541 Jefferson Davis Highway Arlington, Virginia 20362	1		